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U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION I
J.F.K. FEDERAL BUILDING, BOSTON, MA 02203-2211

MEMORANDUM

DATE: February 15, 1990

SUBJ: Requests for Admission; United States v. AVX Corp., et al.

FROM: Mary Sanderson

TO: The File

Mary S.

Attached is a copy of a portion of the Requests for Admission that were served on the United States in January 1987 during the United States of America v. AVX Corporation, et al. litigation proceedings.

Attachment

- 19257 There is no evidence that concentrations of PCBs in the water column in the Acushnet River in New Bedford Harbor exceed 10 micrograms per liter.
- 19258 The EPA concluded that there are too few data for PCBs in fresh water or salt water species to calculate a fresh water or salt water final acute value.
- 19259 The EPA also stated in its report that no chronic tests have been reported in which salt water in vertebrate species were exposed to PCBs.
- 19260 The EPA went on to state that additional chronic data on salt water species for Aroclors may be needed to demonstrate adequately the presence of a relationship between degree of chlorination and chronic toxicity.
- 19261 There is no evidence to support the EPA's water quality criterion for salt water aquatic life.
- 19262 There is no evidence to support a finding that any aquatic life in the Acushnet River has been biologically affected adversely by the concentrations of PCBs in the water or in the sediments.
- 19263 The EPA in establishing the water quality criteria adopted an approach similar to that of the FDA when it established the tolerance levels for PCBs in food. That is, the EPA acted judgmentally and conservatively and prospectively. The EPA determination is not relative to a finding that in fact there have been any injuries to aquatic life from PCBs at the levels found in the Achushnet River in New Bedford Harbor.
- 19264 The polychlorinated biphenyls (PCBs) in the sediments of the Acushnet River estuary (New Bedford, MA) vary widely in both level and composition.
- 19265 Detailed examination of these PCBs by capillary gas chromatography and mass spectrometry (GC and GC/MS) conducted by John F. Brown, Jr. now shows that the original releases consisted of Aroclors 1254 and 1242, probably laid down on the sediments in that order, both rather unevenly.

19266 Since the original deposition, these PCBs have undergone partial extraction into the estuarine waters (at a rapidly declining rate), considerable vertical diffusion within the sediments, and partial dechlorination at subsurface levels. However, they have undergone little or no aerobic microbial biodegradation or horizontal transport between sediment sites.

19267 The dechlorinating agent(s) present, presumably anaerobic bacteria, apparently became established in the north end of the estuary by the late 1950's and have subsequently spread south about 6 Km (to the hurricane barrier) with at least one minor mutation.

19268 The two closely related dechlorination processes (designated H and H') carried out by these agents are distinct from those thus far observed at other PCB spill sites. They are attacking most of the more heavily chlorinated PCB congeners with half-times ranging between about 7 and 50 years, with the pharmacologically active species being among those most rapidly dechlorinated.

19263 Thus, the current fate of the PCBs in the Acushnet estuary sediments is dechlorination, detoxication, slow extraction into the tidal waters, and dissipation into the Atlantic.

19270 The commercial PCB products (e.g., Aroclors) that were so widely released into the environment in past decades possessed one unique feature of chemical composition: These products were complex mixtures of chlorinated biphenyl isomers and homologs (generically referred to as "congeners") that were originally present in fixed relative proportions. The chemical complexity arose because there are many different patterns (theoretically, 209) in which 1 to 10 chlorine atoms can become attached to a biphenyl nucleus. The invariance of original composition occurred because a single manufacturing process, iron-catalysed chlorination of biphenyl to a fixed weight gain, was used by all manufacturers during the entire period of PCB production.

19271 Because of this chemical peculiarity - complex but fixed composition - the commercial PCBs, unlike other environmental contaminants, can preserve a record of

their origin, transformation history, and environmental movement. This happens because the various product grades (classified mainly by weight gain during the original chlorination) each possessed a characteristic distribution of PCB congeners, and because each individual type of transformation process, whether physical, chemical, or biological, attacks the various PCB congeners according to its own selectivity rules, and hence may generate a distinctive new type of congener distribution pattern.

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Thus, given an environmental PCB sample, a determination of its congener distribution pattern, (e.g., by gas chromatography, or GC) may provide information on the original Aroclor released, the nature of the environmental agents that have altered it, and, sometimes also, its route through the environment.

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For many years, little attempt was made to utilize this potentiality. Analysts were well aware that the GC patterns exhibited by PCB specimens recovered from environmental samples rarely gave an exact match with those of their Aroclor standards; however, the differences were difficult to characterize on the low resolution packed column gas chromatograms ordinarily used in analysis. Accordingly, it became the established practice simply to report environmental PCB analyses in terms of whichever Aroclor came closest to the sample in its overall distribution of unresolved congener peaks, and hence could be used as a standard for quantitation.

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Since the availability of high resolution capillary GC techniques, however, substantial progress has been made in both the empirical and chemical characterization of the changes effected by individual transformation processes. Thus, the congener selectivity patterns for the oxidative biodegradation of PCBs by 25 strains of aerobic bacteria isolated from PCB spill sites have been reported. Most or all of these bacteria are believed to effect biodegradation via dioxygenase attack.

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None of the selectivity patterns observed corresponded to that displayed in warm blooded animals, such as humans, where the active enzymes are believed to be monooxygenases of the cytochrome P450 type.

19276 The changes in Aroclor peak distribution pattern resulting from partial vaporization, extraction into water, or adsorption on soils have also been reported.

19277 All of these phase-transfer processes increase the relative concentrations of individual PCB congeners in the less condensed phase in approximate proportion to their volatilities (as indicated by elution rates on a GC column) without the structure-dependent selectivities exhibited by the biodegradation processes.

19278 When the GC patterns of PCBs from heavily contaminated aquatic sediments were examined to see which of the above sorts of alteration patterns might be present, there were observed instead unusual congener distribution patterns, unlike any that had been previously reported.

19273 Patterns that were seen often enough to be sure of their individuality were given letter designations by Dr. Brown in approximate order of their discovery. Further investigation showed that most of these novel patterns, e.g., Patterns B, B', C, and E of the upper Hudson sediments, and Patterns F and G of Silver Lake (Pittsfield, MA) resulted from the occurrence of reductive dechlorination in the sediments, probably mediated by anaerobic bacteria.

19280 The sediments of the New Bedford area, unlike the others under investigation, had been deposited in salt water, and there had already been survey work around the site to define the geographical distribution of the PCBs.

19281 Some of the original analytical chromatograms from the Massachusetts Department of Environmental Quality Engineering, some reprints of published articles showing GC patterns for New Bedford biota and sediments from John Farrington of the Woods Hole Oceanographic Inst. and an extensive collection of chromatograms, originally run by Versar, Inc. on samples collected for EPA, were analyzed.

19282 Examination of these chromatograms indicated that at least two PCB-alteration processes had occurred. The first had effected a partial loss of the lower congener peaks (i.e., those arising from dichlorobiphenyls and

di-orthotrichlorobiphenyls) in most sediments, but particularly those of the outer harbor. The second had produced a sharp decline in the higher congener peaks (mainly those of penta- and hexachlorobiphenyls), particularly in the inner harbor and upper estuary.

19283 The latter alteration suggested possible dechlorination, but the resolution of the analytical GC's did not permit rigorous characterization of either alteration process, and none of the original sediment samples were available. Therefore, the collection and detailed examination of a new set of samples was undertaken

19284 The area selected for study consisted of the upper estuary of the Acushnet River. This is a shallow body of salt water (depth at mean low tide generally 0.2-1.0 m) and surrounding tidal mudflats that is about 2.3 Km long, located between the entrance of the Acushnet (a small stream) at 41°40'37" N and the narrow passage under the Coggeshall St. bridge at 41°39'22" N. This area is thus about 2 Km above (north of) the dock area of New Bedford inner harbor, and about 3.7 Km above the hurricane barrier that forms the boundary between the inner and outer harbors, the latter being alternatively described as either the lower estuary, or an arm of Buzzard's Bay.

19285 Previous sampling studies reported high (>5,000 ppm) PCB levels in parts of the upper estuary, particularly at "shallow" (4-8 cm) depths, albeit in a very "patchy" distribution. The highest PCB levels occurred near the capacitor manufacturing plant located near the northern end of the estuary. This plant is believed (14, 19) to have begun using Aroclor 1254 in substantial quantities in the 1950's, to have switched over most usage to Aroclor 1242 in 1962-65, to have switched again to Aroclor 1016 during 1970-72, and to have used this latter Aroclor until 1978, when all manufacturing use of PCB was banned by law.

19286 The 23 different analytical laboratories which have performed PCB analyses on Acushnet estuary air, sediments, water, and biota have reported their findings in terms of Aroclors 1221, 1232, 1016, 1242, 1248, 1254, and 1260; however, it must be recognized that all of these represented quantitative rather than qualitative analyses, the "Aroclor" or "Aroclors" selected for reporting purposes being merely those that appeared to

serve best as standards for quantitation. Thus, the Brown study was concerned with the original Aroclor composition of the PCBs found in the sediment samples, as well as with their transformation.

19287 Samples were collected from the tidal flats near the low tide line by GHR Analytical Inc. of Lakeville, MA in June, 1986 from 17 sites along the west side of the estuary and six along the east. At each site the surface layers were removed and the two sets of samples taken: Set A at 5-7.5 cm depth and Set B at 15-17.5 cm.

19288 In selecting samples for detailed PCB analysis two of the 17 west side samples that appeared to consist mainly of coarse gravel or cultural artifacts were rejected. The six of the remaining 15 west side sample pairs that permitted the most even spacing of sample sites, along with all six east side sample pairs, were then analyzed.

19289 The selected sediment samples were air-dried, sieved to remove gravel, extracted in a Soxhlet overnight with 1:1 hexane:acetone, evaporated, and the concentrates extracted with concentrated sulfuric acid, mercury, and florisil. All concentrates were then examined by packed column GC (Hewlett Packard 5880 gas chromatograph; 6'x0.25" glass column packed with 1.5% SP2250 and 1.9%SP2401 on Supelcoport) to monitor the success of the cleanup and determine the appropriate loading for capillary GC.

19290 Capillary GC was performed with a Varian 4600 gas chromatograph equipped with an autosampler, splitter/-injector option 1070, a nickel electron capture detector, a Vista 402 data system, and a fused silica capillary column (J&W Scientific, 30m x 0.25 mm I.D., coated with an 0.25u bonded liquid phase of Durabond 1 (DB-1, a cross-linked polydimethylsiloxane). This was operated with an He flow of 30 cm/sec, and a temperature program as follows: 40°C for 2 min; 40° to 80° at 10°/min.; 80° to 225° at 6°/min.; 225° for 10 min.

19291 The mass spectra of the effluent from a DB-1 capillary column (30 m x 0.25 mm I.D.; I u Durabond 1) were determined by positive ion electron impact using a ZAB VG Analytical organic mass spectrometer. Full mass scans of the mass range 50-500 were completed at 2

second intervals, giving approximately 900 low resolution mass spectra per chromatogram when the column was taken through the temperature range 70°-290°C at 8°/min, or about 1600 mass spectra when taken through the range 150°-290°C at 2°/min. The former GC temperature program was found to permit better detecting of weak peaks, the latter greater peak resolution. The mass spectra were used solely to identify the GC peaks of the environmental specimens as indeed arising from PCBs, and to resolve coeluting congeners having different chlorine numbers, since ion fragmentation patterns do not serve to distinguish between PCB isomers.

19292 The response factors (weight PCB per unit area of GC peak) for the electron capture detector (ECD) used were generated for all sizeable DB-1 capillary peaks exhibited by Aroclors 1221 through 1262 by the procedure of Webb and McCall (26); that is, by coulometric determination of weight chlorine per unit area of peak (using a Hall electrolytic conductivity detector from Tracor, Inc.) combined with mass spectrometric determination of homolog ratios and hence weight chlorine per weight PCB in the individual peaks. Response factors for the weaker peaks (which could not be reliably measured with the Hall detector) were estimated from published values.

19293 The chromatograms of the Aroclor standards and sediment extracts observed in this and previous studies have revealed distinguishable peaks at 118 different relative retention times, which have been designated Peaks 1-118. Of these 22 have been further resolved by mass spectrometry, making a total of 140 chromatographically distinguishable congeners or sets of coeluting isomers.

19294 The prior literature reports PCB congener assignments for the GC peaks given by several Aroclors on columns coated with polydimethylsiloxane (e.g., OV-1, SE-30, SE-96), as determined from relative retention times that were mostly calculated from retention indices (23,24); and also assignments for Aroclor 1260 peaks on coatings of SE-54 (6), based on measured relative retention times for all 209 congeners on that coating (21). Because of some disparities among the earlier assignments, Dr. Brown determined the positions of 70 individual congeners with respect to the Aroclor GC patterns on DB-1 by spiking Aroclor standards with specimens of the commercially available synthetic congeners and then

chromatographing. This showed that within isomer sets (distinguishable by GC-MS) the elution sequences on DB-1 closely paralleled those on SE-54, as might be expected from their chemical similarity (pure polydimethylsiloxane vs. copolymer with 5% diphenylsiloxane).

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Dr. Brown was able to make assignments for the generally minor DB-1 peaks not adequately identified by his prior spiking experiments or the prior literature by use of the observed patterns of relative retention on SE-54. This indicated that 180 congeners had retention times close enough to those of the 118 resolvable GC peaks to require consideration as possible components thereof. In 22 cases, however, the mass spectra permitted resolution of non-isomeric coeluting congeners.

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In several cases consideration of the relative proportions of the individual chlorophenyl groups in the particular sample being examined indicated that certain of the coeluting isomers would be present at levels too low to merit reporting as significant peak components. Finally, in one case, that of DB-1 Peak 17, the two coeluting congeners, 2,2',3- and 2,4',6-trichlorobiphenyl, were found to be adequately resolved on the packed column GCs, which contained a slightly more polar coating.

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Individual PCB congeners were designated by Dr. Brown by a terminology paralleling that commonly used in verbal communications; that is by numbers indicating the substitution pattern on each ring separately, separated by a dash. Thus, 2,2',3,4',5,5',6-heptachlorobiphenyl is called 2356-245 CB or simply 2356-245.

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In order to calculate x, the original ratio of Aroclor 1242 to Aroclor 1242 + 1254, and y, the fractional weight loss attributable to evaporative type processes such as true solution, from raw data on the weight fractions of the various PCB congener peaks in the sediment samples and the Aroclor standards, Dr. Brown used an "indicator peak" procedure. In the sample chromatograms, at least two peaks, A and B, can be identified which, after correction if appropriate, can be considered to be unaffected by the chemical transformation(s) underway. If the following parameters are defined:

- a fraction Peak A in sample
- a₁ fraction Peak A in Aroclor 1242 standard
- a₂ fraction Peak A in Aroclor 1254 standard
- b fraction Peak B in sample
- b₁ fraction Peak B in Aroclor 1242 standard
- b₂ fraction Peak B in Aroclor 1254 standard
- c₁ relative effect of evaporative loss on A, i.e.,
 a/a y
- c₂ relative effect of evaporative loss on B, i.e.,
 b/b y

- c relative effect of evaporative loss on A/B ratio

then simple material balances indicate that:

$$(1) \quad a = [(1-c_1y)/(1-y)] [a_1 x + a_2 (1-x)]$$

$$(2) \quad b = [(1-c_2y)/(1-y)] [b_1 x + b_2 (1-x)]$$

$$(3) \quad \frac{a}{b} = \frac{(1-cy) [(a_1-a_2)x + a_2]}{[(b_1-b_2)x + b_2]}$$

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Examination of the chromatograms indicated that congeners 26-34 and 236-34 were probably not being significantly formed or destroyed by the transformation processes at work in the sediments examined, and hence that Peaks 39 (originally mainly 26-34 CB, with a little 236-4 and 234-2) and 61 (originally mainly 236-34 CB, with a trace of 34-34) could be used as indicators for Aroclors 1242 and 1254 respectively. The only correction applied was that the 234-2 in Peak 39 was presumed to be originally present at the 10% level, but to then decline in proportion to any observed decline in Peak 50 (23-34 plus a little 234-4). For these peaks Dr. Brown was able to evaluate the constants in equations 1-3 from Aroclor 1242 and 1254 standards, and from a sample of Aroclor 1242 that had been evaporated to 34% weight loss in the laboratory as follows: a₁, 0.03160; a₂, 0.00789; b₁, 0.00743; b₂, 0.0895; c₁, 0.43; c₂, 10.; c, 0.382.

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Using these values, equations 1-3 were solved for x and y by a process of successive approximations. Examination of the sensitivity of the solutions to variations in the observed parameters a and b indicated no particular magnification of errors in the case of the x values (mainly because the intensity ratios a₁/a₂ and b₂/b₁ are quite large for both peaks). For the y values, however, where 1/(1-y) is roughly proportional to (a+b), errors in a or b could be magnified. As a

check for such errors, Dr. Brown roughly estimated y from the loss in the very strong pair of Aroclor 1242 peaks, Nos. 23 and 24, given by 25-4 and 24-4 CB, and made note of the cases where the calculation via eq. 1-3 had given a questionable result.

19301 The raw data collected during this investigation consisted of SP2250/SP2401 (packed column) and DB-1 (capillary) gas chromatograms, and peak quantitations by weight and mole fractions on the 118 resolvable DB-1 peaks for each of the 24 sediment samples and the Aroclor standards. It also included GC-MS ion chromatograms measured with two different temperature programs (to optimize either sensitivity or resolution) for the standards and for representative samples. All of the DB-1 chromatograms and data print-outs, along with keys to the peak number assignments and congener identifications, are labeled Appendix A, attachment XIX - 6.

19302 Visual inspection of the DB-1 chromatograms revealed a variety of patterns. Some GC patterns (e.g., 9A) resembled that of Aroclor 1242; some (e.g., 18A) were quite similar to Aroclor 1254; most, however, resembled Aroclor 1242-1254 mixtures that had been subjected to either or both of two types of pattern alteration.

19303 The first of these types of alteration consisted of a general, non-selective loss of peaks with short retention times, very similar to that seen when Aroclor 1242 samples were simply allowed to evaporate in the laboratory. There was no hint of the patterns of selective PCB congener removal (i.e., rapid loss of 2-3 and 2-4 CB; slower of 25-2 and 24-2; very slow for 26-2, 26-3, and 26-4 CB) that have been repeatedly observed for aerobic microbial biodegradation by either pure cultures (3,4) or sewage sludge. This observation is consistent with those made at other sites, where PCB pattern alterations resembling those effected by aerobic microbial degradation were often seen in river water, ground water, and soil samples, but only rarely in aquatic sediments.

19304 The second type of alteration consisted of parallel declines in the major peaks 25, 26, 46, 47, 48, 50, 53, 58, 59, 63, 69, 74, 82, 89, 95, 102, and 106, and in many weaker ones as well, along with the increases in peaks, 7, 12, 13, 21, 22, 31, 32, 33, 40, 43, 44, 49,

54, 55, 62, and 88. This pattern of alteration was thus somewhat intermediate between, but clearly distinct from, those previously designated as Pattern B and Pattern F which were seen in many sediment samples of the upper Hudson River (NY) and Silver Lake (Pittsfield, MA), respectively. Accordingly, Dr. Brown concluded that it represented a new type of alteration, and designated it Pattern H.

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Subsequent reexamination of the chromatograms revealed an occasional slightly different pattern, characterized by greater relative declines in Peaks 26, 27, 37, 38, and 45 than with Pattern H; this was designated Pattern H'.

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Attention was then given to the possibilities that the original PCB discharge may have contained Aroclors 1016, 1248, or 1262 rather than just 1242 and 1254. In Aroclor 1242 there is a prominent Peak 50 (mainly 23-34 CB) that is much weaker in Aroclor 1254 and only 1.5% as strong in Aroclor 1016. Thus, in undechlorinated 1242 specimens (such as those of the outer harbor) loss of Peak 50 (relative to indicator Peak 39) can provide a sensitive measure of admixed Aroclor 1016. To extend this method to lightly dechlorinated samples, Dr. Brown found that in the deeper, and hence presumably older (pre-1016), sediments undergoing dechlorination by System H, the disappearance rates for the trichlorobiphenyl component of Peak 25 (mainly 34-2 CB) and for Peak 50 were about equal. Accordingly, he could subtract any percentage loss in Peak 25 trichlorobiphenyls from that in Peak 50, to get an approximate measure of the portion of the Peak 50 loss attributable to admixture with 1016. Application of this procedure to all of the more lightly dechlorinated upper estuary specimens, i.e., samples 2A, 5A, 14A, 17A, 18A, and 18B, indicated an original Aroclor 1016 content of 0-20% in every case.

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In the case of Aroclor 1248, which gives a chromatogram virtually identical to that of 1242 after ca. 50% evaporation, chromatographic proof of presence or absence in admixture with extractively devolatilized Aroclor 1242 would be very difficult. However, the site history indicates no known releases of Aroclor 1248, which was never used in electrical devices. Accordingly, Dr. Brown concluded that the "Aroclor 1248" reportings by previous analysts all represent devolatilized Aroclor 1242 rather than actual 1248.

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Regarding Aroclor 1262, sediment chromatograms showed that the major octachlorobiphenyl peaks (Peaks 109, 110, 112, and 115) were always slightly stronger than in the Aroclor 1254 standard, i.e., with a total weight percent (of Aroclor 1254 content) about 0.3% rather than 0.15%. The excess octachlorobiphenyls were accompanied by only modest proportions of nonachlorobiphenyls (Peaks 113, 114, and 117) indicating the additional Aroclors, if any, to be Aroclor 1260 or 1262 rather than 1268. Since Aroclor 1262 contains 14% by weight of the measured octachlorobiphenyls, the observed increase in octachlorobiphenyls could have been produced by 1% contamination of the 1254 with 1262. Alternatively, it may simply be that the average Aroclor 1254 produced during the period of discharge contained 0.15% more octachlorobiphenyl than did the analytical reference standard.

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The alterations in PCB congener distribution effected by Process H are probably most easily seen in the GC-MS ion chromatograms run under conditions that maximized resolution, even though such tracings lacked a few of the weaker peaks, including those of the mono- and octachlorobiphenyls, which were present only at very low levels.

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The dichlorobiphenyl panels reveal that there has occurred in the sediments a marked increase in Peaks 7, 12, and 13 (2-3, 3-3, and 3-4 CB) relative to the originally prominent Peaks 5, 8, and 14 (2-2, 2-4, and 4-4 CB). There is also a possibility that the latter peaks may all be increased slightly relative to Peak 6 (24- and 25-CB), which is probably the least likely of the group to be either increased or decreased by dechlorination.

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The trichlorobiphenyl tracings show little or no change in the relative levels of Peaks 10, 14, 15, 16, 23, 24, and the component of Peak 17 that elutes earlier on the packed column GC; the congeners responsible for these peaks are 26-2, 25-2, 24-2, 26-3, 25-4, 24-4, and 26-4, respectively. Very prominent increases are shown for the peaks for 25-3 and 24-3 CB, and small increases for 35-2, 34-3, and possibly 35-3 (Peak 27). Marked decreases are seen for Peaks 25, 26, and 38, given mainly by 34-2, 23-4, and 34-4 CB, respectively.

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Among the tetrachlorobiphenyls, the unaffected congeners appeared to be 26-25, 26-24, 236-2, and 236-34. Large increases are seen in 25-25, 25-24, and 24-24, with lesser absolute, though still proportionately important, increases in 24-35, 235-3, and 245-3. The peaks exhibiting 50% decline include those for 245-2, 23-23, 245-4, 25-34, 24-34, 234-3, 23-34 (+234-4), and 34-34. Congeners 23-25 and 23-24 CB show sizeable losses in sediments derived primarily from Aroclor 1242, small losses in most of those with higher Aroclor 1254 content, and an actual gain at one such site (samples 21A, 21B).

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Among the pentachlorobiphenyls, there appears to be little or not net change in the peaks for 236-26, 236-25, 236-23 + 235-25, 235-23, and 235-34 CB, although there may have been a slight increase in 236-25. Unequivocal increases occurred in 246-25, 246-24, 236-24, 245-24, and in Peak 55 (246-34 + 2356-3). All of the other pentachlorobiphenyls declined, with the largest losses being in 245-25, 234-25, 234-24, 234-23, 245-34, and 234-34 CB.

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With the hexachlorobiphenyls, there appears to be little change in 236-236, 235-236, 245-236, 2356-23, or 235-245. The only clear gains are in the minor components 245-246 and 2356-24. All of the other hexachlorobiphenyl peaks declined with the largest absolute losses being in 234-236, 245-245, 2345-25, 234-245, 234-234, and 2345-34.

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Among the heptachlorobiphenyls, there was probably no change in Peak 78 (2356-236 CB); but a clear 30-40% increase in Peak 88 (2345-246 + 2356-245), and clear decreases in all the other congeners. The octachlorobiphenyls were not reliably detected by GC-MS, but were on amplified versions of the DB-1 capillary chromatograms. Because of the uncertainties regarding the octachlorobiphenyl levels in the original discharges, it was not possible to establish their alterability by System H; however, the clear increase in heptachlorobiphenyl Peak 88 suggests that some dechlorination of octachlorobiphenyls had occurred.

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Alteration Pattern H arises from marked decreases in the levels of most of the higher (more heavily chlorinated) PCB congeners, and corresponding increases in some of

the lower congeners, as was seen also for the previously discovered PCB dechlorination systems.

19317 In order to identify the simplest set of dechlorination process steps that would account for this pattern of change Dr. Brown sorted out the congeners responsible for the observed changes according to the types of individual chlorophenyl (CP) groups present. He thus identified as not dechlorinateable by System H groups, 2-, 3-, 4-, 2, 4-, 2, 5-, 2, 6-, 3, 5-, 2, 3, 6-, 2, 4, 6-, and 2, 3, 4, 5, 6- CP on the grounds that there was no clear evidence of decline in any PCB congeners containing only these CP groups. The remaining types of CP groups, namely, 2,3-, 3,4-, 2,3,4-, 2,3,5-, 2,4,5-, 3,4,5-, 2,3,4,5-, 2,3,4,6-, and 2,3,4,5,6-CP, were all identified as potentially reactive to System H on the grounds that one or more PCB congeners containing these CP groups attached to one of the unreactive CP's did show a decline.

19318 Dr. Brown observed that when 2, 3-, 3, 4-, 2, 3, 5-, and possibly 2, 4, 5- CP groups were attached to a CP having two ortho chlorines, as in 2, 6-, 2, 3, 6-, 2, 4, 6-, or 2, 3, 5, 6- CP, there was no longer any reactivity. This phenomenon is reminiscent of the reactivity pattern exhibited by upper Hudson dechlorination Systems B, B', C, and E, where congeners 236-34 and 2356-34 CB showed reduced reactivities, although not as markedly so as towards System H. The effect was not universal, however. PCB congeners containing 2, 3, 4- or 2, 3, 4, 5- CP groups attached to unreactive diortho substituted CP's were still attached by the System H.

19319 The mass balance analyses that were useful in establishing that the compositional changes seen in the upper Hudson and Waukegan Harbor sediments proceeded solely by loss of chlorine atoms located meta or para (rather than ortho) to the other ring could not be strictly applied because of the elutriative losses; however, there was no obvious indication of reduced ortho chlorine content in the dechlorinated products, not any evidence of the marked decline in tri- and tetra-ortho CB's that was exhibited by the ortho-reactive System F.

19320 Accordingly, Dr. Brown tentatively concluded that System H, like the upper Hudson and Waukegan Harbor System is a meta/para-selective dechlorination system. This

conclusion, plus consideration of the relative mole fractions of CP groups lost and gained, permitted identification of the source of the small gain in PCB congeners containing 2-CP groups as 2, 3- CP group dechlorination; of the large gain in congeners containing 3- CP's as 3, 4- CP loss; of the occasionally increased 2, 3- CP as 2, 3, 4- (also conceivably 2, 3, 5-) loss; of the sizeable 2, 4- CP gain as 2, 3, 4- (plus conceivably 2, 4, 5-) loss; of the large 2, 5- CP gain as 2, 4, 5- (plus the smaller 2, 3, 5-) loss; of the occasionally increased 2, 3, 5- CP as 2, 3, 4, 5- CP loss; and of the small but unequivocal gains in congeners containing 3, 5- or 2, 4, 6- CP groups as 3, 4, 5- or 2, 3, 4, 6- CP dechlorinations, respectively.

19321 The extent to which this set of conclusions is supported by the various observations of PCB congener level change is set forth in Table 1, Attachment XIX-7. This Table shows that a simple stepwise matching between congener loss and congener gain is frequently precluded by the fact that the congener that is the product of one dechlorination step may still be the substrate for another; however, there are still enough unequivocal observations to define a self-consistent pattern.

19322 In order to estimate relative dechlorination rates for the various chlorophenyl groups, Dr. Brown first determined the number of half-losses (calculated as $-\log_2$ of the fraction of the original congener level still present) for various penta-, hexa-, and heptachlorobiphenyls (which are primarily derived from Aroclor 1254) in sediments showing well-advanced Aroclor 1254 dechlorination. Dr. Brown then did the same for the reactive tri- and tetrachlorobiphenyls (which are primarily derived from Aroclor 1242) in sediments where Aroclor 1242 dechlorination was prominent. He then presumed, on the basis of the mean values shown in Table 3, attachment XIX-8 that in sediments where the dechlorinations of Aroclor 1254 and 1242 were equally advanced the reductions in Peaks 50 (mainly 23-34 CB) and 58 (234-25 CB) would be about equal. This permitted the estimates of the relative reactivities for all of the major PCB congeners shown in Table 2, Attachment XIX-9.

19323 Table 2 shows that PCB congener reactivity toward dechlorination System H is determined not only by the arrangement of chlorine atoms on the presumably reactive CP group, but also by their arrangement on the other,

presumably unreactive, CP group, where ortho (2 and/or 6) substituents appear particularly important in reducing reactivity. Table 2 also shows that the minor dechlorination system, H', differs from H in exhibiting higher reactivities for 2, 3-, 2, 3, 5-, and 2, 3, 6- CP groups, relative to the rest of the pattern.

19324 The resistance to dechlorination of 26-34 and 236-34 CB, congeners which give rise to prominent peaks in Aroclors 1242 and 1254, respectively, meant that these peaks could be used to estimate the original Aroclor 1242-1254 ratios by the "indicator peak" method described in the experimental section. Likewise, the identification of Peaks 50 and 58 (prominent in Aroclors 1242 and 1254, respectively) as containing only easily dechlorinated congeners (i.e., 23-34 plus a little 234-4 CB and 234-25 CB, respectively) meant that the declines in these peaks could be used as indicators of the dechlorination states of the two Aroclors.

19325 The resulting compositional data are presented, along with information on site locations and total levels for oils and PCBs, in Table 3. This table lists the site numbers for samples taken along either the west or east side of the estuary in either the first or second column, respectively, and in the same order as the north-to-south sequence of sites; thus the arrangement of the site numbers within the first two columns also constitutes a rough map of the relative positions of the sites.

19326 From Table 3, the following findings are noted. The usual range of estuarine bottom textures (mud, sand, gravel, and marsh bed in various proportions) was represented. No measurements of oxygen levels were made, but it was noted that the sediments after drying generally graded in color from the black of FeS to the brown of Fe₂O₃ upon moving from north to south over the range studied. The odor of H₂S was apparent in the samples denoted "soft black mud," indicating that they, at least, were anoxic. There were no obvious correlations between either PCB level or alteration state and sediment textures.

19327 There was a general tendency for the A and B (shallow and deep) specimens at each side to be similar in color, texture, and odor; in levels of both oils and PCBs; in the calculated 1242:1254 ratios, extractive losses, and

dechlorination indices; in the dechlorination pattern; and also in the patterns of minor, non-PCB peaks on the chromatogram. These similarities occurred despite much wider variations between sites in all of these parameters, and hence suggest that both the oils and the Aroclors had been undergoing vertical diffusion within the sediments at most sites.

19328 The Metcalf & Eddy summary of previous sampling data also noted wide site-to-site variations in PCB level in the upper estuary. In addition, however, this compilation suggested that PCB levels there were highest at "shallow" (4-8 cm) depths, corresponding to Dr. Brown's depth "A", somewhat lower at the "surface" (0-4 cm), and one to two orders of magnitude lower in the "deep" (>8 cm) layers, which would correspond to Dr. Brown's depth "B". This latter generalization is in clear discord with the data shown in Table 3. For all sites examined, the average total PCB levels at depths A and B were 1187 and 839 ppm, respectively, indicating a mean B-depth (15-17.5 cm) PCB level only 29% lower than at depth "A") 5-7.5 cm).

19329 Despite the diffusive blurring of the stratification, it was possible to see three compositional differences between the PCBs at depths A and B: (a) at every site where the PCB levels were high enough for reliable peak area measurements, the Aroclor 1242:1254 ratio was similar to or larger in the upper ("A") sample than in sample B, suggesting that the Aroclor 1242 deposition came generally later than that of Aroclor 1254. (b) Again at every site with PCB peaks strong enough for reliable comparison, the extent of dechlorination, whether of the Aroclor 1242-derived Peak 50 (23-34 CB), or of the 1254-derived Peak 58 (234-25 CB) was equal to or greater in the "B" (lower) sample than in "A", indicating that the dechlorination was occurring preferentially in the lower layers, as in the upper Hudson sediments. (c) At both "A" and "B" depths, the dechlorination was more advanced in the Aroclor 1254-derived peak in the more northerly (upriver) sites, and more advanced in the Aroclor 1242-derived peak in the more southerly sites, indicating that seeding with the dechlorinating agent occurred before the time of Aroclor 1242 deposition at the former sites, and after that time in the latter.

19330 Prior to collecting the upper estuary samples for DB-1 capillary GC analysis, a careful study of the Versar and

Woods Hole chromatograms was made by Dr. Brown to identify features indicative of compositional change.

19331

The sediment samples analyzed by Versar included 72 grab samples collected by GCA/Technology Division for EPA throughout the New Bedford area and surrounding waterways in August 1982 and 72 upper estuary core sections similarly collected in January 1983, as well as sediments taken from sewage lines and sewer overflow areas. The analyses were done by conventional packed column GC on a polydimethylsiloxane column. Dr. Brown observed the chromatograms of the Aroclor standards, which accompanied those of the sediments, to be very similar in general appearance to those reported by Webb and McCall. Accordingly, he used the Webb and McCall peak designations (which describe retention times relative to DDE=100 for peaks obtained on an isothermal (195°C) SEC-30 packed column) for denoting the Versar GC peaks seen. Such packed column peaks rarely represent individual PCB congeners; instead they correspond to unresolved aggregates of the peaks seen on polydimethylsiloxane-coated capillary columns, such as DB-1. The correspondence between the packed column and DB-1 peak numbers is given in *Table 4*, Attached XIX -

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19332

The Versar chromatograms of the various sediments showed all of the low resolution peaks seen in the Aroclor 1242 and 1254 standards, but with often sizeable differences in relative peak heights, and occasionally slight differences in the apparent relative retention time (RRT). In virtually all cases the peaks with RRT 21, 28, 32, and 40 were clearly depressed relative to the very strong peak at RRT 37 (which corresponds to Peak 21-24 on Fig. 1). In the tetrachlorobiphenyl region there was usually enhancement of the peak at RRT 47, and depression of those at RRT 54 and 78. In the penta- to hexachlorobiphenyl region, some GC patterns showed the peaks at RRT 84, 125, 146, and 174 at the same relative peak heights as in the Aroclor standards, whereas others showed a marked "high end drop-off," meaning that the observed pattern of relative peak height became 84>125>146>174. (The pentachlorobiphenyl peaks at RRT 96 and 104 were not observable on the Versar GC's because DDE, RRT=100, had been added to all samples as an internal standard.) This was a sufficiently unambiguous feature of the packed column chromatograms to permit the GC's of sediments that contained >1 ppm PCB to be scored for "high end drop-off." This scoring was done before Dr. Brown had the key indicating the

relationship between the separate sets of identification numbers used by the sampler and the analyst.

19333 When the key became available, a striking geographic correlation emerged: all of the samples collected in the estuary north of the hurricane barrier showed the "high end drop-off" feature in their chromatograms, whereas this feature was not detectable in the samples from any of the other marine collection sites: e.g., those in the lower estuary, south of the hurricane barrier, those in Clark's Cove, or in the surrounding areas of Buzzard's Bay. The only other sediment chromatograms exhibiting the "high end drop-off" feature were those of a small group of otherwise 1254-like specimens that were collected in a short section of the East Rodney French Blvd. (ERFB) sewer line near David St. The effluent from this line ultimately discharges into the outer harbor.

19334 Correlation of the packed column and capillary chromatograms showed that the packed column peaks at RRT 84, 125, 146, and 174 must be produced mainly by the congeners responsible for DB-1 Peaks 51-54, 69, 74-75, and 82 respectively, indicating that a sample that had undergone dechlorination by Ssystem H or H' would indeed exhibit the observed "high end drop-off" in the packed column GC. However, because of the lower resolution of the packed column chromatograms Dr. Brown cannot exclude the possibility that the dechlorination system operating in the middle estuary (e.g., inner harbor) or in the ERFB sewer line may have been of a subtype different from H or H'.

19335 Brownawell and Farrington have published SE-30 capillary gas chromatograms for two sections (3-5 and 35-45 cm) taken from a single outer harbor core collected in September, 1983. Standards indicate that these two PCB samples resembled a simple mixture of Aroclor 1254 with evaporated 1242 and virtually pure Aroclor 1254, respectively. The accompanying plots of peak height data for intermediate core sections showed a nearly smooth decline with depth for the Aroclor 1242:1254 ratio.

19336 Measurements on the published chromatograms indicated that for the upper sediment sample the peak corresponding to DB-1 peak 50 had a height of $103 \pm 5\%$ of that in the Aroclor 1242 standard, both measured

relative to peak 39, indicating that no detectable Aroclor 1242 dechlorination or admixture with Aroclor 1016 had occurred. However, the Peak 58 heights were depressed 37% and 8% relative to the Aroclor 1254 standard in the upper and lower sediments respectively, indicating some deposition of dechlorinated 1254 (possibly from the ERFB sewer line) in the upper sample. The 3-5 cm sediment GC also showed small losses in congeners 105 and 138, corresponding to DB-1 peaks 74 and 82 (234-34 and 234-245 CB), and a small gain in peak 54 (245-24 CB), consistent with, but not unambiguously demonstrative of, Pattern H. None of these small changes would have been large enough to produce an observable "high end drop-off" in the packed column GC.

19337 Water samples collected from just south of the hurricane barrier in September, 1982, were reported to contain approximately half their PCBs in true solution and half as suspended particulates. This report shows a pair of DB-5 capillary gas chromatograms for dissolved and suspended PCB fractions of a water sample collected at ebb tide. Dr. Brown noted that the GC of the dissolved fraction resembled that a partially dechlorinated Aroclor 1242 with marked enhancement of dichlorobiphenyl peaks 5 and 7 and/or 8, (2-2 and 2-3 and/or 2-4 CB, while that of the suspended particulates looked more like the sort of lightly dechlorinated 1242-rich Aroclor 1244-1254 mixture seen in some of the least altered "A" level sediments from the upper estuary (e.g., 2A) except for the absence of all dichlorobiphenyl peaks. Relative peak height measurements indicated the losses in the Aroclor 1242-derived Peak 50 to be 44 and 20%, and those in the Aroclor 1254-derived Peak 58 to be 42 and 41% in the dissolved and suspended fractions, respectively. The losses for both these peaks averaged 67% (1.6 half-clearance) in the upper estuary sediments (Table 3). Thus, the levels of Aroclor 1242 and 1254 dechlorination in the water at the north end of the outer harbor at ebb tide were intermediate between those of the upper estuary sediments and those of the outer harbor.

19338 The Woods Hole group reported chromatograms of mussels (Mytilus edulis), green crab (Neopanope taxons) and lobster (Homarus americanus) from about the same location. The mussel PCBs resembled an Aroclor 1242 + 1254 mixture, but with those peaks that are most sensitive to System H dechlorination (e.g., DB-1 peaks 25, 26, 50, 58, 59, and 74, corresponding to 34-2, 23-4, 23-34, 234-25, 234-24, 234-23, and 234-34 CB) largely

removed. These same peaks were also largely removed from the chromatograms of the lobster and crab, along with those of all PCB congeners lacking in 4,4'-substitution. Thus, the GC pattern of the residual PCBs in the lobster showed strong peaks for 245-34, 245-245, and 245-234, and medium ones for 24-4, 24-24, 245-4, 24-34, and 245-24 CB. In the crab, there was much additional loss of congeners other than 245-245 CB; 245-34 was down by a half, and 245-4, 24-34, 245-24, and 245-234 still more so.

19339 These PCB congener-persistence patterns are quite similar to those seen in the human and indicate that the two crustaceans, unlike the mussel, possess active eukaryotic P450 cytochrome systems for metabolizing lipophilic xenobiotics.

19340 The chromatograms of flounders (Lephopsetta maculata and Pseudopleuronectes americanus) from the same area were not published, but were stated to be intermediate in appearance between those of the mussels and lobsters implying the presence of a P450 cytochrome system, but at lower levels. Because of the biodegradative activities thus exhibited by the crabs, lobsters, and flounder, it is not certain whether the sharply reduced levels of System H-sensitive congeners, such as 23-34, 234-25, 234-24, 234-23, and 234-34, that were seen in their tissues resulted from reductive dechlorination in the sediments or oxidative metabolism in the animal; however, their reduced levels in the mussels are clearly relatable to dechlorination.

19341 This investigation by Dr. Brown resulted in the accumulation of a body of very detailed compositional information (in the form of quantitated capillary gas chromatograms) on the PCBs in upper Acushnet estuary sediments, and also provided more limited compositional information on those of other sediment, biota, and water samples from the New Bedford area.

19342 The PCB congener distributions observed in individual samples permitted deductions as to the original Aroclor compositions of the PCB releases, and the transformation processes that subsequently occurred. Comparison between the Aroclor compositions and transformation states of the PCBs in different samples permit deductions as to PCB diffusion and translocation, and the timing of the observed dechlorination processes.

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Previous investigations of PCBs in freshwater sediments, e.g., those of Lake Superior, Lake Michigan, and the Upper Hudson have shown good preservation of stratification, indicating very little vertical mobility for the PCBs. In sharp contrast, the 12 pairs of samples showed no large compositional differences between the 5-7.5 cm and 15-17.5 cm levels for any of the 7 parameters listed in Table 3, strongly suggesting diffusive blurring of stratification. Also suggestive of vertical diffusion are the various reports indicating PCB levels in the sediment surface layers to be equal or nearly equal to those in the subsurface, despite the cessation of significant PCB releases, the continuation of active sedimentation, and losses of PCBs to the water column.

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So, the vertical diffusivity of the PCBs demonstrates that all of the PCBs now in the sediments may be able to reach those anaerobic layers where dechlorination is proceeding.

19345

During and shortly after the period of active discharges the rate of PCB extraction into the water column must have been between 10- and 100-fold greater than at present, and that the elution rate has been dropping sharply since that time.

19346

There are two obvious mechanisms by which PCBs might move from one patch of sediment to another. One would be by scouring and redeposition of sediment particles carrying bound PCBs. The other would be dissolution into and readsorption from the water column. The available evidence, however, indicates that neither translocation process has been occurring to a significant extent in the Acushnet. This evidence is of two types. First, both we (Table 3) and others have observed an extraordinarily spotty distribution of both Aroclor 1242 and 1254 in the upper estuary sediments, with many instances of 1000-fold concentration differences between nearby sites. Second, there are virtually none of the dechlorinated PCBs, which are ubiquitous in the sediments located north of the hurricane barrier, in those located south of it. Neither observation would be possible if there had been any significant horizontal transport between sediment banks, by whatever mechanism.

19347 This current immobility of the PCBs now present in Acushnet estuary sediments suggests that the PCBs, which are heavy, water-insoluble oils, were originally released to the estuary in the form of suspended droplets, and that these droplets moved various distances before sinking into the sediments. This would result in a rather spotty deposition on the sediments, the deposition pattern for each release being determined by the location of the discharge point and the state of the tide. Once adsorbed onto the sediment particles, however, little further horizontal movement between sediment sites could occur except by scouring and redeposition, which require higher water flow rates than normally occur in the estuary.

19348 The inability of PCBs to move from one sediment bank to another, by whatever mechanism, along with the observed differences in composition, means that there must have been separate sources for the PCBs found in the sediments of the upper estuary, Clarks Cove, and the outer harbor.

19349 The results show that the upper and middle Acushnet Estuary PCBs are undergoing dechlorination by at least two closely related dechlorination systems, herein designated H and H', which can be characterized in detail as to their relative reactivities toward the various individual PCB congeners present in the Aroclor mixtures released.

19350 In Table 4, Dr. Brown summarizes the derived information on chlorophenyl group reactivities for System H, and shows comparable summaries for two other dechlorination systems: System B, which is one of four meta/para PCB-dechlorinating systems (B, B', C, and E) found in upper Hudson River sediments and System F, which is one of two ortho/meta/para PCB dechlorinating systems (F and G) found in the sediments of Silver Lake (Pittsfield, MA). Also included in Table 4 is a list of the reported electrochemical reduction potentials of the various chlorophenyl groups, not because of any evidence that the environmental dechlorinations proceed by simple electron transfer reactions, but simply because these reduction potentials represent the only currently available indicators of the intrinsic chemical reactivities of the various chlorophenyl groupings toward reductive processes.

19351 Table 4 shows that the susceptibility of chlorophenyl groups to attack by System H (indicated by "R" rather than "-" in Column H of the Table) does correlate to a fair extent with this index of reactivity, and also with the reactivity pattern shown by System F. Moreover, the pattern of chlorophenyl groups that appear in the dechlorinated product is also similar to that of System F. The intrinsic chemical reactivity, or reduction potential, of the agent responsible for System H must be quite similar to that responsible for F, and roughly equivalent to that of an Hg-Pt electrode set at -1.94 volts (relative to a standard calomel electrode in dimethyl sulfoxide). The equivalent potential for System H' may be slightly more negative, judging from the greater reactivity towards the borderline groups 2,3- and 2,3,6-CP.

19352 The relative reactivities of the various PCB congeners towards Systems H and H' are clearly influenced by structural, or steric, effects as well as intrinsic susceptibilities to reduction. There would appear to be three sorts of steric effects involved: First, hindrance at the ortho (2 or 6) position by the opposite ring, regardless of chlorination pattern. As a result, there is a meta/para-selective dechlorination, like those of the upper Hudson River, rather than the ortho/meta/para dechlorinations of Silver Lake Systems F and G. Second, hindrance by additional ortho substitution on the reacting ring. Thus, groups 2-, 2,3,6-CP and 2,3,5,6- are progressively less reactive than 2,3-CP; and 2,3,4,6- and 2,3,4,5,6-CP are less reactive than 2,3,4-CP.

19353 This effect may be particularly significant when the ortho chlorine is located opposite the meta chlorine that is to be removed; thus, the reactivity of 3,4-CP is undepressed in 2,3,4-CP, but significantly so in 2,4,5-CP, and the same relative positioning (3 vs. 6, or 5 vs. 2) is also present in 2,3,6- and 2,3,5,6-CP. The third steric effect, shown by the vertical progressions in Table 4, is a general reduction in reactivity produced by substituents on the opposite ring, particularly when in ortho (2 or 6) positions.

19354 The first and third of these steric effects are also exhibited by System B (and the other upper Hudson systems as well), but the second is unique to H and H'. It would appear that removal of a chlorine from position 3 by System H is inhibited by the presence of a chlorine

in position 6, whereas for Systems B, B', or C the inhibition is greater if the blocking chlorine is in position 5. At any event, System H is more reactive than B to 2,3,4-, 2,3,5-, 2,3,4,5-, and possibly also 2,3,4,6-CP groups, but less reactive to 2,4,5-, 2,3,6-, 2,3-, 2,4-, and 2,5-CPs. As a result of this reactivity pattern, an Aroclor that has undergone dechlorination by this system will develop the characteristic pattern of GC peak gains and losses that we have termed Pattern H: prominent declines in the peaks of almost all congeners containing 3,4-, 2,3,4-, 2,3,4,5-, or 3,4,5-CP groups, and corresponding increases in those containing 3-, 2,4-, 2,5-, or 3,5-CPs.

19355 In the U.S., the PCBs were widely used in the manufacture of electrical devices for nearly fifty years (1930-1978) without generating any findings of significant health effects. Concern over PCB toxicity arose in the 1970's after reports of widespread human poisoning in Japan caused by ingestion of rice oil ("yusho") that had been contaminated by PCBs. Eventually, further analyses of the rice oil identified polychlorinated dibenzofurans as the toxic contaminants, and the indictment of PCBs was withdrawn.

19356 All of the congeners that are of primary toxicological concern in rats are among the group that is most rapidly attacked by System H and H'. All those congeners that are of secondary toxicological concern are either also among this group or among those that are only slightly less rapidly attacked. Thus, an Aroclor mixture being transformed by System H or H' will undergo loss of pharmacologically active congeners (detoxication) much faster than the overall rate of dechlorination.

19357 An exact estimate of the extent of detoxication is somewhat complicated by the fact that the two congeners of greatest concern, 34-34 and 234-34 CB, both coelute with other, non-isomeric congeners on DB-1 capillary columns, so that the less reliable GC-MS data (e.g., Fig. 3) rather than the GC-ECD measurements (e.g., Figure 2) must be used for their quantitation. These data, along with the reactivity patterns of Tables 2 and 4, do show, however, that the toxic congeners are being removed at least as rapidly as the Peaks 50 and 58 that have routinely been used as indicators of dechlorination status. On this basis, Table 3 shows detoxication of at least 90% (3.3 half-clearances) in sediments 17B, 19B, and 22B) or at least 67% (1.6 half-clearances) averaged

over all of the upper estuary sediment samples collected. The similar levels of toxic congener loss that occur in the mussels, crabs, and lobsters collected south of the hurricane barrier in the outer harbor are somewhat easier to observe, since the DB-5 gas chromatograms that were reported provide greater separation of the 234-34 CB peak (IUPAC 105) from nearly congeners than does the DB-1 column that we used.

19358 The dechlorinating agents are enzymes, presumably each associated with a specific strain of anaerobic bacteria. No PCB-dechlorinating bacteria have yet been isolated, nor is early success in such an endeavor likely, in view of the experimental difficulties normally attendant upon work with environmental anaerobes. However, it has been demonstrated through use of microbial inhibitors that the analogous dechlorinations of chlorobenzoic acids and chlorophenyls are microbially mediated, and the same approach has recently been found to show that PCB dechlorination by upper Hudson sediments is also dependent upon microbial action. Thus, agents H and H' are microbial.

19359 The dechlorinase enzymes H and H' are clearly much more closely related to each other than to those of the other dechlorination systems found to date. This suggests the possibility that agents H and H' may be mutant varieties of the same microbial species.

19360 PCB-containing sediments that were not undergoing dechlorination as of the time of observation were seen downriver of the actively dechlorinating patches in both the upper Hudson and the Acushnet. All of these observations suggest localized population blooms of otherwise very rare environmental bacteria.

19361 It is a stoichiometric necessity that if some chemical species is being reduced, as the PCBs are when dechlorinated, some other species must be oxidized. Thus, the anaerobic bacteria that effect dechlorination must be using the PCBs as oxidizing agents (e.g., terminal electron acceptors) in their metabolic processes. This is strongly allowed on thermodynamic grounds; in fact, the free energy gain in oxidizing glucose (for example) to carbon dioxide and water using PCBs as the oxidants is calculated to be about three times that available from sulfate. Thus, the rare anaerobic bacterial strain that happens to possess

enzyme systems that can effect PCB dechlorination should be at a selective advantage, and would be expected to proliferate. What is notable about the Acushnet dechlorinating strains H and H' is that they were able to compete with the endogenous sulfate-utilizing anaerobes even in estuarine sediments, where the sulfate level was found to be almost as high as in seawater.

19362 The possible period for significant Aroclor 1254 release as between 1945 and 1965, and that for Aroclor 1242 as between 1962 and 1972. There is no detectable Aroclor 1016 (in manufacturing use 1970-78) in the sediments.

19363 In order to estimate the absolute rates of System H dechlorination from this chronology, two presumptions are made. The first is that the dechlorination process, once past the induction period, proceeded according to first order kinetics. The second is that the intrinsic reactivities of the Aroclor 1242-associated Peak 50 (mainly 23-34 CB) and the Aroclor 1254-associated Peak 58 (234-25 CB) are about the same. This is the same presumption as that previously used in deriving a single scale for Table 2, and is based upon the identity of the mean numbers of half-clearances of these two peaks, when averaged over all sites listed in Table 3.

19364 The first presumption means that all of the "numbers of half-clearances" listed on the last three columns of Table 3 are equivalent to the numbers of half-times that the dechlorination has been proceeding. Thus, in the most advanced sediments of the northern end of the upper estuary, e.g., 17B, 19B, and 22B, Peak 58 (and also those of the other Aroclor 1254-associated 234-XY CBs) has undergone about 3.5 half-times of clearance.

19365 The second presumption means that in these more northerly sediments there was an approximately one half-time time lapse between the time of initiation of the Aroclor 1254 dechlorination and the mean arrival time of Aroclor 1242 in the subsurface zone where dechlorination was occurring (last column, Table 3). If one conservatively estimates the mean time of deposition of the Aroclor 1242 as roughly 1966, and the sample was collected in 1986, this means that the 2.5 half-times of dechlorination that elapsed after the arrival of the 1242 in the dechlorination zone took 20 years, if there was no transit time between deposition and arrival, or perhaps 15 years if there was a 5-year delay during

which downward diffusion and/or burial occurred, indicating respective values of 8 and 6 years for the half-time. Consideration of the observed variances and uncertainties in the values used in this calculation indicates that the $t_{1/2}$ for Peak 58 (234-25 CB) removal in actively dechlorinating sediments should be estimated as 7 ± 3 years.

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This number is equivalent to giving the period of active dechlorination of the sediments used for determining the relative rate data of Table 2 as 25 ± 10 years. Thus, the actual dechlorination $t_{1/2}$ for any of the individual congeners listed in Table 3 can be determined by dividing 25 ± 10 by the number of half-clearances given in the Table.

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All such $t_{1/2}$ values refer to sediment strata where dechlorination is actively progressing. However, it is very likely that there may be a thin layer at the surface that is too aerobic for anaerobic bacterial growth. For the PCBs in this zone to dechlorinate, they must diffuse down into the active layers. Table 3 indicates that relative to the presumably fully active lower ("B") layer, the extent of dechlorination was 20-25% lower in the upper ("A") layer, or about 10-15% lower for the average of the two, which is probably representative of the average for the sediment column as a whole. Thus, while the clearance $t_{1/2}$ for species like 234-25 CB in the active layers of the sediments can be stated as 7 ± 3 years it probably should be stated as 8 ± 3 years for the whole of the PCBs present.

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The differences in the relative extents of dechlorination of the Aroclor 1254-derived peaks (last column, Table 3) can be used to sketch out a chronology of events. First, there were sizeable releases of Aroclor 1254 on various occasions within the period 1945 to 1965. Next, organism H appeared in PCB-adapted form, probably near the north end of the estuary. It was probably established in several locations, e.g., sampling sites 17, 19, and 22, by the late 1950's; in the remainder of the northern half of the upper estuary (with the probable exception of site 18) by the time of the switchover to Aroclor 1242 (1962-65), and in most sites in the southern half of the upper estuary during the mid-1960's.

19369 Either a second seeding or mutation occurred, giving organism H'. This became established in one small area near sites 9 and 12, which are within 100m of each other. Also during this period a limited seeding of the Aroclor 1254 deposits in the EREB sewer line occurred, possibly via sewage overflow connections that permit reverse flow into the sewer system during periods of high water levels.

19370 Sizeable releases of Aroclor 1242 to the upper estuary presumably then occurred on various occasions within the period 1962-1971, along with continued colonization of subsurface sediment layers by anaerobe H. In the absence of capillary GC data one cannot say when H reached the inner harbor; only that as of the time of the GCA sampling (1982-83) dechlorination was well along at all sites north of the hurricane barrier, but not to the south.

19371 Presuming that all sediments north of the hurricane barrier are now seeded with the agent responsible for System H (or H') dechlorination, and that this dechlorination will continue to proceed in the future as it has over the past years, Dr. Brown was able to project its future course. The projection takes into account the facts that the commercial Aroclors that were released into the estuary were complex mixtures of PCB congeners having quite different dechlorination rates. Those congeners that actually produce toxic effects or unusual enzyme inductions in animals, notably, those containing only 3,4-, 2,3,4-, 3,4,5-, and 2,3,4,5-CP groups attached to each other, are also the groups most rapidly attacked by System H (Table 2).

19372 Attachment XIX-11 is a list of references on which Dr. Brown relied in his study.

19372A -Annexed hereto as Attachment XIX- 12 is a true and accurate copy of a report of L. David Maxim, Ph.D. It is a report prepared by an authority in the field and is generally relied upon by experts. (Hereinafter the Maxim Report).

19373 Polychlorinated Biphenyl (PCB) is the name given to a series of chemical compounds produced industrially by chlorination of biphenyl with anhydrous chlorine and iron filings or ferric chloride as a catalyst.